About the Book

Welcome to "Environmental Chemistry," a thorough examination of the intricate relationship between chemical processes and the environment. This book explores the fundamental principles, applications, and implications of environmental chemistry, offering insights into the dynamic interplay between human activities and the natural world.

In the opening chapter, "Fundamentals of Environmental Chemistry," readers establish a foundation for understanding environmental systems, including pollutant sources, reactions, and fates.

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Arun Sharma is currently serving as Associate Professor in the department of chemistry at Career Point University, Kota (Rajasthan). His fields of research are electrochemistry, material science, immunosensors, quantum dots and warfare agents. He obtained his Ph.D. in Chemistry from Jiwaji University Gwalior (NAAC A++), in 2016.

Dr. Erum Gull Naz is a famous researcher in theoretical and computational chemistry, specializing in chemical reaction dynamics, rate constants, thermodynamics, and kinetics. She earned her Ph.D. at the prominent Indian Institute of Technology (IIT) in Jodhpur, Rajasthan. Her study also includes organo-physical chemistry and interstellar chemistry, which investigate basic processes that occur on Earth and beyond.

Surabhi Singh, a visionary leader having exemplary research, academic, & administrative experience in the field of Higher Education, obtained her Ph.D. in Environmental Chemistry from Career Point University, Kota (Rajasthan). Currently, she is serving as Associate Professor cum Head of Department of School of Basic and Applied Sciences at Career Point University, Kota (Rajasthan).

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Ms. Insha Ara, a researcher in theoretical and analytical chemistry, specializing in organic chemistry. She earned her Master of Science at the prominent Career point University in Kota , Raj where she studied many aspects of chemical processes, such as their Analytical and practical and get a Gold medalist in academics and got many certificates in academic

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Preface

Welcome to "Environmental Chemistry," a thorough examination of the intricate relationship between chemical processes and the environment. This book explores the fundamental principles, applications, and implications of environmental chemistry, offering insights into the dynamic interplay between human activities and the natural world.

In the opening chapter, "Fundamentals of Environmental Chemistry," readers establish a foundation for understanding environmental systems, including pollutant sources, reactions, and fates.

Chapter 2, "The Impact of Various Environmental Pollutants on the Earth's Atmosphere," illuminates diverse pollutants affecting air quality and climate dynamics.

"Thermodynamic Principles and Applications in Engineering," Chapter 3, explores thermodynamics' role in environmental processes and engineering solutions, emphasizing energy considerations in sustainability efforts.

Chapter 4, "Biochemical Kinetics: Exploring Gibbs Free Energy and Enzyme Catalysis," focuses on biological transformations' mechanisms and relevance to environmental systems.

Chapters 5 through 8 delve into atmospheric chemistry, examining processes leading to inorganic and organic particulate matter formation, thermochemical and photochemical reactions, and their implications for atmospheric composition and climate change.

Chapter 9, "Green Chemistry for Water: Sustainable Solutions to Pollution," addresses the nexus between chemistry and water quality, proposing innovative approaches for mitigating pollution and promoting sustainable water management.

Lastly, Chapter 10, "Soil Chemistry," explores chemical dynamics within terrestrial ecosystems, including soil pollution, nutrient cycling, and human activities' impact on soil health.This multidisciplinary journey deepens our understanding of environmental chemistry's role in addressing contemporary challenges and fostering sustainable solutions for our planet's well-being.

We extend our heartfelt thanks to Pramod Maheshwari, Sir, Managing Director and Chairman of Career Point University, Kota, as well as the HOD and Dean for their inspiration and support during the book's development. Gratitude is also expressed to our families for their constant encouragement, and to students and the teaching community for their support. Suggestions to improve the book's quality are welcomed.

Dr. Arun Sharma

Dr. Erum Gull Naz

Dr. Surabhi Singh

Ms. Kriti Tripathi

Ms. Insha Ara

Environmental Chemistry

Syllabus

Unit-I (Dr. Arun)

Stoichiometry, Gibb's energy, Chemical potential, Chemical equilibria, acid-base. reactions Solubility product, solubility of gases in water, the carbonate system, unsaturated and saturated hydrocarbons, Radio nuclides.

Unit -II (Dr. Surabhi)

Classification of elements, chemical speciation, Particles, ions and radicals in the atmosphere. Chemical processes for formation of inorganic and organic particulate matter. Thermochemical and photochemical reactions in the atmosphere

Unit - III (Dr. Erum)

First law of thermodynamics, enthalpy, adiabatic transformations, second law of thermodynamics, Carnot's cycle, entropy.

Unit - IV (Dr. Erum)

Gibbs free energy, chemical potential, phase equilibria, Gibbs Donnan equilibrium, third law of thermodynamics, enzymes catalysis, Michaelis/Menten equation.

Unit - V (Ms. Kriti Tripathi)

Oxygen and ozone chemistry, Chemistry of air pollutants, Photochemical Smog, Chemistry of water, concept of D.O., B.O.D., and C.O.D, water treatment : Sedimentation, Coagulation, Filtration, tertiary and advanced treatment, redox potential. Inorganic and organic components of soil, nitrogen pathways and NPK in soils.

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Dr. Arun Sharma, Dr. Erum Gull Naz

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About the Author's:

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CHAPTER 7

Thermochemical and Photochemical Reactions in the Atmosphere

Dr. Surabhi Singh & Insha Ara

ABSTRACT

This abstract explores the intricate interplay of thermochemical and photochemical reactions in the Earth's atmosphere, elucidating their pivotal roles in atmospheric chemistry. Thermochemical reactions, driven by thermal energy, play a crucial role in atmospheric processes such as combustion and the release of volatile organic compounds. These reactions contribute to the transformation of primary pollutants and the formation of secondary pollutants, impacting air quality and human health. On the other hand, photochemical reactions, initiated by solar radiation, govern the intricate chemistry of ozone formation, photolysis of pollutants, and the production of radical species. The interdependence of these thermochemical and photochemical processes shapes the composition and reactivity of the atmosphere, influencing global climate patterns and radiative forcing. This abstract underscores the significance of understanding the synergistic effects of thermal and solar-driven reactions for accurate atmospheric modeling, environmental monitoring, and the development of effective strategies for mitigating air pollution and climate change. As we navigate a rapidly changing world, continued research in this field remains essential for unraveling the complexities of atmospheric chemistry and its far-reaching implications on the Earth's ecosystems and human well-being.

Content-

1. Introduction

The Earth's atmosphere is a dynamic chemical reactor, where a myriad of thermochemical and photochemical reactions continuously shape its composition and govern its intricate behavior. Thermochemical reactions, fueled by thermal energy, and photochemical reactions, initiated by solar radiation, collectively influence the atmospheric processes that impact air quality, climate, and environmental sustainability (Finlayson-Pitts & Pitts, 2000). Understanding these reactions is pivotal for unraveling the complex interactions between natural and anthropogenic compounds in the atmosphere.

Thermochemical reactions encompass processes such as combustion, oxidation, and thermal decomposition, contributing to the transformation of pollutants and the formation of secondary atmospheric constituents. Concurrently, photochemical reactions involve the absorption of solar

radiation, leading to electronic transitions and the formation of reactive intermediates, influencing the fate of various atmospheric species (Jacob, 1999).

This introduction sets the stage for an exploration of the multifaceted world of thermochemical and photochemical reactions in the atmosphere, emphasizing their integral roles in atmospheric chemistry (Seinfeld, J. H., & Pandis, 2016). By delving into the mechanisms and implications of these reactions, we gain insights into the intricate web of processes shaping the Earth's atmospheric composition and behavior (Stocker, et al. (Eds.). 2013).

This introduction provides a foundation for exploring the intricate world of thermochemical and photochemical reactions in the atmosphere, highlighting their crucial roles in shaping the environmental and climatic conditions of our planet.

2. Thermochemical Reactions In The Atmosphere

Thermochemical reactions in the Earth's atmosphere constitute a fundamental aspect of atmospheric chemistry, influencing the composition and reactivity of the air we breathe. These reactions, driven by thermal energy, encompass a wide array of processes that play a crucial role in shaping atmospheric dynamics and air quality (Seinfeld, J. H., & Pandis, 2016). From combustion processes releasing pollutants to the thermal decomposition of volatile organic compounds, thermochemical reactions have profound implications for both natural and anthropogenic contributions to the atmospheric chemical composition.

Thermochemical reactions are intricately linked to the life cycle of pollutants, affecting their transformation and fate in the atmosphere ((Jacob, 1999). Understanding these reactions is essential for accurate atmospheric modeling, pollutant dispersion predictions, and the formulation of effective This introduction sets the stage for delving into the complex realm of thermochemical reactions in the atmosphere, emphasizing their significance in understanding atmospheric processes and their subsequent impact on air quality and environmental health (Finlayson-Pitts & Pitts, 2000).

a) Various Steps of Thermochemical Reactions in the Atmosphere:

Combustion Processes: Thermochemical reactions associated with the combustion of fossil fuels and biomass release a plethora of pollutants, including nitrogen oxides (NOx) and sulfur dioxide (SO2). These reactions are influenced by temperature, fuel composition, and oxygen availability (Stocker, et al. (Eds.), 2013).

Volatile Organic Compound (VOC) Degradation: Thermochemical degradation of VOCs involves the breaking of chemical bonds at elevated temperatures. This process leads to the release of reactive intermediates, influencing atmospheric oxidation processes (Atkinson, 2000).

Oxidation of Atmospheric Particles: Thermochemical reactions contribute to the oxidation of atmospheric particles, influencing their size, composition, and lifetime. This process plays a crucial role in the formation and transformation of aerosols in the atmosphere (Zhang, 2010).

Thermal Decomposition of Nitrogen Species: Thermochemical reactions involving the thermal decomposition of nitrogen species contribute to the release of reactive nitrogen compounds, influencing the nitrogen cycle and contributing to the formation of nitrogen oxides (Crutzen, 1970).

Photolysis and Thermal Reactions in Tropospheric Ozone Formation: Thermochemical reactions, coupled with photolysis processes, contribute to the complex chemistry of tropospheric ozone formation. Understanding these reactions is crucial for assessing ground-level ozone concentrations (Finlayson-Pitts & Pitts, 2000).

These steps highlight the diverse and intricate nature of thermochemical reactions in the atmosphere, underscoring their importance in atmospheric chemistry, air quality, and climate dynamics.

b) Applications of Thermochemical Reactions in the Atmosphere:

Air Quality Management: Thermochemical reactions, particularly those involved in the combustion of fossil fuels, significantly contribute to the formation of air pollutants. Understanding these reactions is crucial for developing effective strategies for air quality management (Seinfeld & Pandis, 2016).

Climate Change Mitigation: The study of thermochemical reactions aids in understanding the sources and transformation of greenhouse gases, contributing to climate change. Strategies to mitigate climate change often involve controlling emissions from thermochemical processes (Stocker, et al. (Eds.)., 2013).

Pollutant Fate and Transport Modeling: Thermochemical reactions influence the fate and transport of pollutants in the atmosphere. Atmospheric models incorporating these reactions help predict the dispersion and transformation of pollutants, aiding in environmental impact assessments (Jacob, D. J. (1999).

Renewable Energy Production: Thermochemical reactions are fundamental in various renewable energy processes, such as solar thermal systems and biomass energy production. Understanding these reactions is essential for optimizing energy conversion processes (Tester., et al. 2012).

Chemical Composition of Atmospheric Aerosols: Thermochemical reactions contribute to the chemical composition of atmospheric aerosols. Studying these reactions aids in characterizing aerosol properties, which have implications for climate, air quality, and human health (Zhang, 2010).

: **Green Chemistry and Sustainable Practices:** Thermochemical reactions play a role in the development of green chemistry and sustainable practices, aiming to reduce the environmental impact of chemical processes. Understanding thermochemical reactions is crucial for designing eco-friendly chemical processes (Anastas & Warner, 1998).

These applications highlight the diverse and significant roles of thermochemical reactions in addressing environmental challenges, ranging from air quality and climate change to sustainable energy production and green chemistry initiatives.

3. Photochemical Reactions In The Atmosphere

Photochemical reactions in the Earth's atmosphere represent a dynamic and intricate set of processes driven by solar radiation, playing a crucial role in shaping atmospheric composition and influencing various environmental phenomena. Solar energy initiates photochemical reactions that lead to the transformation of numerous atmospheric constituents, affecting air quality, climate, and

the overall chemistry of the atmosphere (Finlayson-Pitts, & Pitts, 2000). This introduction provides an overview of the key concepts surrounding photochemical reactions in the atmosphere, emphasizing their significance in understanding the complex interactions between sunlight and atmospheric constituents.

Solar radiation is a primary driver of photochemical reactions, initiating a cascade of transformations that impact both natural and anthropogenic components of the atmosphere (Crutzen, 1970). These reactions involve the absorption of sunlight by molecules, leading to electronic transitions and the formation of reactive intermediates. Understanding photochemical processes is essential for unraveling the atmospheric lifecycle of pollutants, the formation of secondary pollutants such as ozone and aerosols, and their subsequent implications for air quality and climate (Seinfeld, & Pandis, 2016).

This introduction sets the stage for a deeper exploration of the multifaceted world of photochemical reactions in the atmosphere, emphasizing their pivotal role in atmospheric chemistry and their far-reaching implications for the Earth's environment.

a) Various Steps of Photochemical Reactions in the Atmosphere:

Photon Absorption and Electronic Excitation: Photochemical reactions begin with the absorption of solar radiation by atmospheric molecules. This leads to electronic excitation, where electrons move to higher energy levels (Finlayson-Pitts & Pitts, 2000).

Formation of Excited States and Reactive Intermediates: Excited molecules formed during photon absorption become reactive intermediates. These species possess higher energy and increased reactivity, initiating subsequent photochemical transformations (Jacob, 1999).

Ozone Formation through Photolysis of O2: Solar radiation, particularly ultraviolet (UV) light, drives the photolysis of molecular oxygen (O2) in the stratosphere, resulting in the formation of ozone (O3) (Seinfeld, & Pandis, 2016).

Photolysis of Nitrogen Dioxide (NO2): Photolysis of nitrogen dioxide (NO2) by solar UV radiation generates nitrogen oxide radicals (NO and NO2), influencing the nitrogen cycle and contributing to the formation of tropospheric ozone (Crutzen, 1970).

Formation of Hydroxyl Radicals (OH): Hydroxyl radicals (OH) are key reactive species formed through the photolysis of water vapor in the atmosphere. OH radicals play a critical role in the oxidation of various atmospheric pollutants (Finlayson-Pitts & Pitts, 2000).

Photodissociation and Aerosol Formation: Photodissociation of precursor molecules can lead to the formation of reactive fragments, contributing to the nucleation and growth of atmospheric aerosol particles (Zhang, 2010).

Understanding these steps in photochemical reactions is essential for deciphering the intricate chemistry of the atmosphere, assessing the impacts of solar radiation on air quality, and comprehending the complexities of atmospheric processes.

b) Applications of photochemical Reactions in the Atmosphere

Photochemical reactions play a crucial role in the Earth's atmosphere, contributing to various processes that impact air quality, climate, and environmental chemistry. Here are some key applications of photochemical reactions in the atmosphere:

Ozone Formation and Depletion: Photochemical reactions in the stratosphere lead to the formation and depletion of ozone. Ozone formation involves the photolysis of oxygen molecules (O_2) to form ozone (O_3) through reactions like $O_2 + UV \rightarrow O + O$, followed by $O + O_2 \rightarrow O_3$ (Crutzen, 1970).

Smog Formation: Photochemical smog is formed in urban areas through the interaction of sunlight with pollutants such as nitrogen oxides (NOx) and volatile organic compounds (VOCs), leading to the formation of ground-level ozone and other harmful oxidants (Finlayson-Pitts & Pitts 1997).

Global Atmospheric Chemistry: Photochemical reactions contribute to the cycling of various chemical species in the atmosphere, affecting the composition and chemistry on a global scale. This includes reactions involving methane, carbon monoxide, and other greenhouse gases (Seinfeld & Pandis, 2016).

Photodissociation of Water Vapor: Photodissociation of water vapor in the upper atmosphere is crucial for understanding the water cycle and the production of hydroxyl radicals (OH), which play a significant role in the removal of various atmospheric pollutants (Sander, et al., 2011).

Photolysis of Halocarbons: Photochemical reactions involving halocarbons in the atmosphere contribute to the release of halogen radicals, which play a role in ozone depletion and influence the atmospheric oxidation capacity (Solomon, 1986).

These references provide foundational information on the applications of photochemical reactions in the atmosphere. Further research articles and textbooks in atmospheric chemistry can offer more in-depth insights into specific reactions and their implications.

4. Conclusion

In conclusion, the interplay between thermochemical and photochemical reactions in the Earth's atmosphere forms the intricate tapestry of atmospheric chemistry, profoundly influencing air quality, climate dynamics, and environmental health. Thermochemical reactions, driven by thermal energy, contribute to the transformation of pollutants, the oxidation of volatile compounds, and the formation of inorganic particulate matter. Simultaneously, photochemical reactions, initiated by solar radiation, govern processes such as ozone formation, photolysis of pollutants, and the production of radical species. The synergistic effects of these reactions shape the chemical composition of the atmosphere, influencing its reactivity and radiative properties.

Understanding the mechanisms and implications of thermochemical and photochemical reactions is essential for accurate atmospheric modeling, climate change assessments, and effective air quality management. As humanity faces the challenges of a changing climate and escalating air pollution, ongoing research in this field remains crucial. By unraveling the complexities of these reactions, we can pave the way for informed strategies to mitigate the impacts of atmospheric changes, safeguard human health, and foster sustainable environmental practices. The intricate balance between thermochemical and photochemical processes underscores the interconnectedness of Earth's atmospheric systems, emphasizing the need for interdisciplinary collaboration to address the multifaceted challenges posed by our evolving atmosphere.

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